

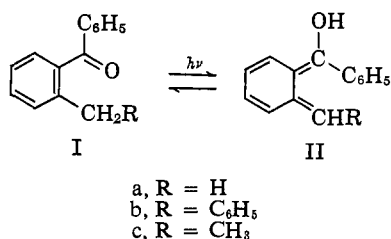
# Photoenolization of Some Photochromic Ketones. The Scope and Mechanism of the Reaction

K. R. Huffman, M. Loy, and Edwin F. Ullman

Contribution from the Chemical Department, Central Research Division,  
American Cyanamid Company, Stamford, Connecticut. Received August 4, 1965

Photochromism has been observed among a number of aromatic ketones which include derivatives of 2-benzyl-3-benzoylchromones and 2-benzyl-3-benzoyl-4-quinolones. At reduced temperatures *o*-methyl- and *o*-benzylbenzophenone, 6-benzylbenzanthrone, and 3-benzyl-2-benzoylbenzofuran are also photochromic. The photochromic behavior is shown to occur by a photoenolization process in which the triplet of the photoenol is probably an intermediate. Photoenolization was unexpectedly inhibited at 77°K. in a saturated hydrocarbon glass but was reactivated in some cases by certain electron-donor additives. These and other polarizable additives activated long-lived phosphorescence among some of the ketones that did not enolize at 77°K. The results suggest that the reaction proceeds through an  $n,\pi^*$  triplet of the ketone which must pass through an activation energy barrier on enolization. Intersystem crossing of certain ketones also seems to have a low-temperature energy barrier. The failure of several of the compounds studied to undergo photoenolization is examined in the light of the proposed mechanism.

In connection with a study of the phenomenon of photochromism we have undertaken to prepare compounds which will change color on exposure to ultraviolet radiation and will spontaneously return to their original color in the dark. One process that might be expected to produce photochromic behavior is the photoenolization of  $\alpha,\beta$ -unsaturated ketones bearing an appropriately disposed aliphatic hydrogen at the  $\gamma$ -position.<sup>1,2</sup> It had, in fact, already been shown that potentially colored enols IIa and IIb (no stereochemical implication intended) were formed reversibly on irradiation of *o*-methyl- and *o*-benzylbenzophenones<sup>1</sup> (Ia and Ib). Although absorption due to II is not observable by steady irradiation of solutions of I at room temperature, flash photolysis of Ib in cyclohexane produced a spectroscopically observable species re-



garded as the enol IIb which had a lifetime of about 10 sec.<sup>3</sup> Thus it should be possible by suitable modification of I to produce longer lived colored enols which

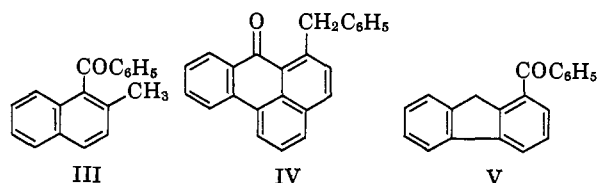
could be observed and studied by more conventional techniques.

Indeed Beckett and Porter<sup>4</sup> have recently reported that on flashing isopropyl alcohol solutions of Ia or Ic long-lived yellow species are formed to which they assigned the enol structures IIa and IIc. However, the long lifetime of these species in the hydroxylic solvent as compared to the short lifetime of the presumed enol IIb in a hydrocarbon solvent casts doubt on the validity of this interpretation.<sup>5</sup>

In order to shed more light on these observations and to investigate more fully the scope of the photoenolization process and the chemistry of the resulting enols, a study of some potentially photoenolizable ketones has been made. The present paper describes the preparation and photochemical properties of such ketones in which structural modifications have been made to increase the lifetime of the enol forms. In the following paper<sup>6</sup> consideration is given to the detailed photochemistry of two of these compounds.

## Results

Our first attempt to produce long-lived photoenols involved the study of the aromatic ketones 1-benzoyl-2-methylnaphthalene<sup>7</sup> (III), 6-benzylbenzanthrone<sup>8</sup> (IV), and 1-benzoylfluorene<sup>9</sup> (V). Since enolization of III



and IV would interrupt the aromatic resonance of one ring of a naphthalene system, whereas enolization of I interrupts a more highly resonance stabilized benzene nucleus, loss of resonance stabilization on enolization should be less for III or IV than for I and the enol forms of III and IV should be relatively more stable. The enol of V likewise should have enhanced stability, due in this case to added delocalization, as compared to II. In point of fact, however, irradiation of solutions of these compounds even when using a very high intensity source (1000-w. B-H6 high-pressure mercury arc) gave no color at room temperature, which indicated that either photoenolization was not occurring or the reketonization rate was still much greater than the photoenolization rate.

(1) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961).  
(2) N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).  
(3) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2671 (1963).

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).  
(5) For a more recent interpretation of these observations see E. F. Ullman and K. R. Huffman, *Tetrahedron Letters*, 1863 (1965).  
(6) W. A. Henderson, Jr., and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5424 (1965).  
(7) F. Mayer and A. Sieglitz, *Ber.*, **55**, 1835 (1922).  
(8) C. F. H. Allen and S. C. Overbaugh, *J. Am. Chem. Soc.*, **57**, 740 (1935).  
(9) N. Campbell and A. Marks, *J. Chem. Soc.*, 2941 (1951).

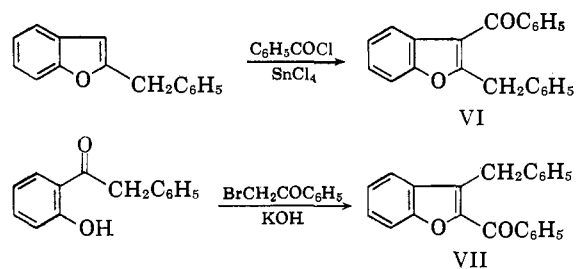


Figure 1.

The lack of color on irradiation of the benzanthrone IV was shown not to be due to the failure of the photoenolization reaction. Thus upon irradiation of an ethanol-ether glass containing this compound at 77°K., where the reketonization reaction should be suppressed, a strong deepening of the original yellow color was produced which was reversed on warming, a phenomenon previously reported for *o*-benzylbenzophenone<sup>10</sup> (Ib) and also observed in this study for *o*-methylbenzophenone (Ia). Moreover, irradiation of a benzene-deuteriomethanol solution of IV led to deuterium exchange on the methylene group as shown by a diminished intensity of the methylene peak in the n.m.r. at  $\tau$  5.10. By contrast, photoenolization of III or V apparently did not occur, since neither compound gave color changes even at low temperature or underwent photoinduced deuterium exchange. We conclude therefore that the absence of color on irradiation of solutions of III, IV, and V at room temperature was due to the failure of III and V to undergo photoenolization and to the occurrence of an extremely high rate of reketonization of the enol of IV.

In order to further reduce the loss of aromatic resonance energy on photoenolization and hence decrease the reketonization rate, the benzoylbenzylbenzofurans VI and VII were next studied. Both of these compounds (syntheses shown in Figure 1) underwent deuterium exchange on irradiation in a deuteriomethanol solution. The 2-benzoyl-3-benzylfuran (VII) exchanged about twice as rapidly as the isomeric VI. While these compounds also failed to give a color on irradiation at room temperature in solution, the more photosensitive, VII, gave a transient yellow color when irradiated at temperatures below  $-50^\circ$  in ether or isopropyl alcohol, indicating a probable increase in the stability of the photoenol over those of the earlier studied compounds.

In principle, much greater stabilization of the photoenols could be achieved by positioning a carbonyl group so as to permit its involvement in hydrogen bonding with the enolic hydrogen. A possible structure that might allow this to occur is the chromone VIII which might on enolization give the hydrogen-bonded enol IXa. However, a potential difficulty lay in the necessary rotation of the benzoyl carbonyl grouping *after* internal abstraction of a hydrogen atom, a process which probably would have to occur as a result of the initial photochemical activation, since a subsequent *cis-trans* isomerization of an initially unrearranged enol IXb probably would not compete with reke-

(10) J. D. Margerum, *et al.*, *J. Phys. Chem.*, **66**, 2434 (1962).

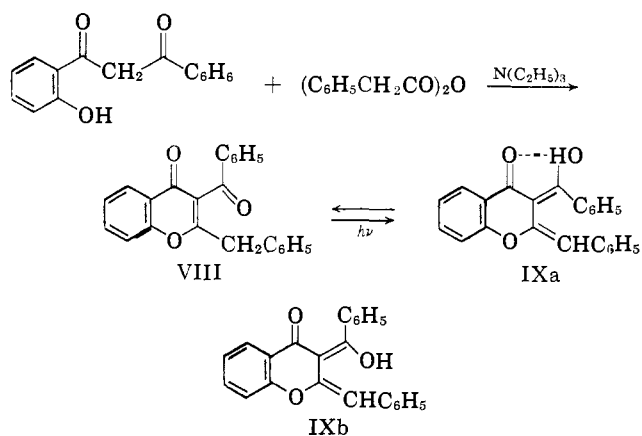


Figure 2.

tonization.<sup>11</sup> Nevertheless, an indication that this problem might not be encountered was found in an observation by Collie that crystals of 3,5-diacetyl-2,6-dimethyl-4-pyrone became lemon yellow on exposure to sunlight and that the color disappeared on melting or dissolution in a solvent.<sup>12</sup>

The preparation of the chromone VIII, which is based on analogy with the synthesis of other 3-acylchromones,<sup>13</sup> is given in Figure 2. Exposure of initially colorless solutions of this compound to ultraviolet light at room temperature caused the rapid formation of a colored species ( $\lambda_{\text{max}}^{\text{C}_6\text{H}_6}$  460  $\mu$ ) which ranged in appearance from yellow to red depending on the color intensity. The color was found to fade in only a few seconds in polar solvents such as ethanol or acetonitrile, but to persist in nonpolar solvents such as benzene for periods of several hours in the absence of oxygen.<sup>14</sup>

Three lines of evidence support the assignment of the enol structure IXa to the colored species.<sup>15</sup> First, irradiation of a deuteriomethanol solution of the chromone VIII led to exchange of the methylene protons as shown by the diminution of the n.m.r. peak at  $\tau$  6.06. Second, the infrared spectrum of an irradiated benzene solution of VIII after subtraction of the absorption due to VIII displayed weak new bands at 6.23 and 6.56  $\mu$ , consistent with the absorption expected by a hydrogen-bonded enolized  $\beta$ -diketone. Third, the effect of various reagents on the rate of fading was completely consistent with the enolized  $\beta$ -diketone structure. Thus the fading process was greatly accelerated by small amounts of base such as triethylamine and partially inhibited by acids such as acetic or benzenesulfonic acids. This behavior is consistent with a base-catalyzed ketonization process, IXa  $\rightarrow$  VIII. Moreover, nickel acetate was even more effective than acids in retarding the rate of fading in alcohols, as might be expected by the well-known ability of this metal to coordinate with appropriately disposed enolized  $\beta$ -

(11) Related considerations have been applied to a possible light-induced internal hydrogen transfer reaction of *o*-hydroxybenzophenone: G. S. Hammond, N. J. Turro, and P. A. Leermakers, *ibid.*, **66**, 1144 (1962).

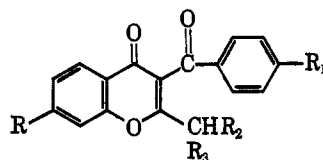
(12) J. N. Collie, *J. Chem. Soc.*, **85**, 971 (1904).

(13) W. Baker, J. B. Harborne, and W. D. Ollis, *ibid.*, 1294 (1952).

(14) For details of the fading process, see ref. 6.

(15) Additional evidence based on trapping of the photoenol will be presented in a forthcoming paper.

Table I. 3-Aroyl-2-methylchromones



Compd.	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Reactn. time, hr.	Yield, %	M.p., °C.	Formula	Anal., %					
									Calcd.		Found			
								C	H	N	C	H	N	
VIII	H	H	C <sub>6</sub> H <sub>5</sub>	H	1.5 <sup>a</sup>	62 <sup>b</sup>	121–123	C <sub>22</sub> H <sub>16</sub> O <sub>3</sub>	81.61	4.74		80.83	4.78	
X	H	H	<i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	H	1.0 <sup>a</sup>	15 <sup>a</sup>	182–183	C <sub>24</sub> H <sub>18</sub> O <sub>4</sub>	77.82	4.90		78.02	4.91	
XI	H	H	<i>p</i> -C <sub>6</sub> H <sub>4</sub> OH	H	3.0 <sup>d</sup>	55 <sup>b</sup>	210.5–211.5	C <sub>22</sub> H <sub>16</sub> O <sub>4</sub>	77.51	4.53		77.35	4.71	
XII	H	CN	C <sub>6</sub> H <sub>5</sub>	H	16.0 <sup>a</sup>	45 <sup>c</sup>	187–188.5	C <sub>24</sub> H <sub>15</sub> NO <sub>3</sub>	78.89	4.14	3.83	79.04	4.47	4.15
XIII	H	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	H	1.5 <sup>a</sup>	21 <sup>c</sup>	204.5–206.5	C <sub>23</sub> H <sub>15</sub> NO <sub>3</sub>	71.68	3.92	3.64	71.22	3.98	4.04
XIV	H	H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	16.0 <sup>a</sup>	37 <sup>b</sup>	157–158	C <sub>29</sub> H <sub>20</sub> O <sub>2</sub>	83.63	4.84		84.06	4.74	
XV	N(CH <sub>3</sub> ) <sub>2</sub>	H	C <sub>6</sub> H <sub>5</sub>	H	8.0 <sup>a</sup>	29 <sup>b</sup>	185–186	C <sub>26</sub> H <sub>21</sub> NO <sub>2</sub>	78.31	5.52	3.65	78.49	5.37	3.43
XVI <sup>e</sup>	H	H	H	H	0.25 <sup>a</sup>	61 <sup>f</sup>	115.5–116.5	C <sub>17</sub> H <sub>12</sub> O <sub>3</sub>						
XVII	H	H	H	Br	5.0 <sup>g</sup>	70 <sup>b</sup>	147–148	C <sub>17</sub> H <sub>11</sub> BrO <sub>3</sub>	59.50	3.23	23.28 <sup>h</sup>	59.38	3.53	23.82 <sup>h</sup>
XVIII	H	H	H	SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2.0 <sup>i</sup>	35 <sup>f</sup>	175–178	C <sub>23</sub> H <sub>16</sub> O <sub>5</sub> S	68.30	4.00	7.93 <sup>i</sup>	68.18	4.20	7.80 <sup>i</sup>

<sup>a</sup> Synthesis analogous to that given in Figure 2. <sup>b</sup> Recrystallized from ethanol. <sup>c</sup> Recrystallized from benzene. <sup>d</sup> HBr treatment of X. <sup>e</sup> See ref. 13. <sup>f</sup> Recrystallized from ethanol-water. <sup>g</sup> N-Bromosuccinimide treatment of XVI. <sup>h</sup> Br analysis. <sup>i</sup> Sodium benzenesulfonate treatment of XVII. <sup>j</sup> S analysis.

diketones.<sup>16</sup> Addition of bromine to a colored solution led to the rapid disappearance of the color, a behavior which was also consistent with the enol formulation.

In addition to VIII, several derivatives of VIII were prepared by procedures analogous to that given in Figure 2. These compounds are listed in Table I. Each of these compounds also displayed photochromic properties with the exception of 2-benzyl-3-*p*-nitrobenzoyl-, 2-methyl-3-benzoyl-, 2-bromomethyl-3-benzoyl-, and 2-phenylsulfonylmethyl-3-benzoylchromone (XIII, XVI, XVII, and XVIII, respectively), which were not photochromic even at low temperatures. In accord with the apparent inability of these latter compounds to undergo photoenolization, the nitro and methyl derivatives XIII and XVI also failed to undergo light-induced deuterium exchange while an exchange study on the sulfone XVIII was precluded by its ready photodecomposition. The bromo compound was not studied.

Quinolone analogs of VIII were also examined for their ability to undergo photoenolization. 2-Benzyl-3-benzoyl-4(1H)-quinolone (XIX) was prepared by a method similar to that reported for the preparation of the known 2-methyl-3-benzoyl-4(1H)-quinolone<sup>17</sup> (Figure 3), for which no light sensitivity has been reported.

Compound XIX was converted into three methylated derivatives. Treatment with methanolic diazomethane gave a methyl ether XX which was characterized by the absence of quinolone carbonyl absorption in the infrared and by an O-methyl signal in the n.m.r. at  $\tau$  6.18. By contrast, methylation of XIX by addition of its sodium salt to excess methyl iodide gave a second methyl derivative which by its spectral similarity to XIX (C=O absorption at 6.30  $\mu$ ) and n.m.r. methyl absorption at  $\tau$  6.40 was assigned the N-methyl structure XXI. When excess base was used and methyl iodide was added to the reaction mixture, the dimethyl

derivative XXII was obtained. The similarity of the infrared and ultraviolet spectra of XXII to those of XXI together with the appearance of two methyl peaks in the n.m.r. at  $\tau$  6.58 (singlet) and 8.24 (doublet) and a peak due to the single tertiary hydrogen coupled to methyl at 5.52 (quartet) confirmed this structure.

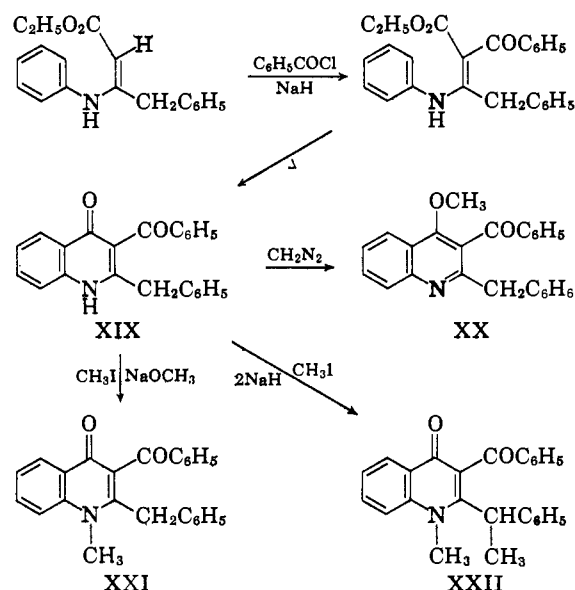


Figure 3.

Irradiation of each of these quinolones in solution at room temperature resulted in strong color formation by the two N-methyl derivatives XXI and XXII. However, no color was formed on irradiation of solutions of the parent compound XIX or the O-methyl derivative XX either at room temperature or at 77°K. Deuterium exchange studies were in accord with the assumption that the photochromic behavior was diagnostic of photoenolization. Thus, the N-methylbenzylquinolone XXI exchanged deuterium on irradiation in the presence of deuteriomethanol whereas the nonphotochromic parent compound XIX failed to exchange.

(16) See, for example, C. M. Harris and S. E. Livingstone in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p. 101.

(17) G. Singh and G. V. Nair, *J. Am. Chem. Soc.*, **78**, 6105 (1956).

Both of the photochromic derivatives become intensely colored on irradiation in benzene solution and faded over several hours in the dark.

### Mechanistic Evidence and Discussion

A summary of the spectral, deuterium exchange, and photochromic properties of the compounds studied is given in Tables II and III. While perhaps the only

Table II. Spectral and Photochemical Data for Potentially Photoenolizable Ketones

Compd.	Ultraviolet maxima in CH <sub>3</sub> OH, m $\mu$ (log $\epsilon$ )	D-ex-change
Ia	252 (4.18), 278 (3.69), 332 (2.18) <sup>a</sup>	+
Ib	251 (3.95) 332 (2.15)	+ <sup>b</sup>
III	224 (4.84), 251 (4.14), 277 (3.78), 321 (3.01)	-
IV	232 (4.67), 237 (4.62), 255 (4.36), 272 (4.15), 282 (4.02), 304 (3.94), 340 (3.65), 357 (3.90), 389 (3.97)	+
V	255 (4.53), 263 (4.54), 287 (3.81), 320 (3.34)	-
VI	243 (4.36), 276 (3.93), 283 (3.91)	+
VII	232 (3.99), 260 (3.91), 318 (4.27)	+
VIII	225 (4.40), 250 (4.36), 295 (3.93), 303 (3.89)	+
X	226 (4.50), 252 (4.34), 295 (3.99), 305 (3.90)	c
XI	226 (4.50), 251 (4.35), 295 (4.00), 304 (3.92)	c
XII	227 (4.40), 250 (4.43), 287 (4.00), 304 (3.91)	c
XIII	227 (4.49), 265 (4.38), 293 (4.16), 303 (4.06)	-
XIV	248 (4.33), 295 (3.90), 305 (3.85)	c
XV	264 (4.54), 293 (3.93), 354 (4.24)	c
XVI	221 (4.45), 250 (4.40), 293 (3.91), 302 (3.86)	-
XVII	235 (4.40), 246 (4.40), 301 (3.91)	c
XVIII	232 (4.45), 257 (4.34), 298 (4.01), 307 (3.99)	d
XIX	239 (4.59), 318 (4.15), 328 (4.06)	-
XX	226 (4.72), 250 (4.37), 317 (3.32)	d
XXI	242 (4.54), 250 (4.52), 325 (4.16), 338 (4.10)	+
XXII	243 (4.53), 250 (4.51), 325 (4.09), 337 (4.09)	c

<sup>a</sup> R. F. Rekker and W. Th. Nauta, *Rec. trav. chim.*, **80**, 747 (1961). Ethanol was used as solvent. <sup>b</sup> Reference 1. <sup>c</sup> Not studied. <sup>d</sup> Compound decomposed.

Table III. Photochromism of Potentially Photoenolizable Ketones<sup>a</sup>

Color <sup>b</sup> obsd. at 25°C. and 77°K.	Color obsd. at 77°K. but not at 25°C.
VIII (460), X (473), XI (470), XIV (449)	Ia, Ib, IV, VII
Color <sup>b</sup> obsd. at 25°C. but not at 77°K.	Color not obsd. at 25°C. or 77°K.
XII (460), XV <sup>c</sup> (446), XXI <sup>c</sup> (498), XXII <sup>c</sup> (472)	III, <sup>d</sup> V, <sup>d</sup> VI, XIII, XVI, XVII, XVIII, XIX, XX <sup>c</sup>

<sup>a</sup> Measurements at 25°C. in benzene and at 77°K. in a 1:1 ether-ethanol glass. <sup>b</sup> Visible absorption maxima (m $\mu$ ) of benzene solutions of the colored forms at 25°C given in parentheses. <sup>c</sup> Strong phosphorescence observed at 77°K. in ether-ethanol glass. <sup>d</sup> Strong phosphorescence observed at 77°K. in both ether-ethanol and 3-methylpentane-methylcyclohexane glasses.

completely reliable test for photoenolization is light-induced deuterium exchange, photochromism was observed in all but one of the compounds that was shown to undergo deuterium exchange, and that compound, the benzofuran VI, exchanged only relatively slowly. Thus, the observed photochromism within this series of compounds is taken to indicate that photoenolization can occur, although the absence of photochromism taken alone may only indicate that photoenolization is quite inefficient.

Of particular interest in terms of understanding this reaction are the eight compounds that fail (III, V, XIII, XVI, and XIX) or probably fail (XVII, XVIII, and XX) to undergo photoenolization. Since data have previously been described which suggest that the photoenolization of *o*-benzylbenzophenone proceeds by way of an n, $\pi^*$  triplet,<sup>8</sup> the possibility was entertained that some of the present compounds failed to photoenolize because their lowest excited state configurations were  $\pi,\pi^*$  rather than n, $\pi^*$  triplets. An attempt was therefore made to determine if any change in the ability of these compounds to undergo photoenolization could be achieved by using nonpolar solvents which would be expected to lower the energies of the n, $\pi^*$  relative to the  $\pi,\pi^*$  states.<sup>18</sup> Since deuterium exchange studies in a nonpolar medium were not feasible, the photochromic phenomenon was used to indicate photoenolization.

If this hypothesis were correct, some of the inert compounds might be expected to become colored in a hydrocarbon solvent, particularly if the temperature were sufficiently low to prevent thermal reketonization. It was thus most surprising to find that *none* of the compounds in this study became colored in a 3-methylpentane-methylcyclohexane glass at 77°K. even though inhibition of photochromic behavior was not observed in this medium at room temperature! Further examination of this phenomenon revealed that photochromism at low temperatures was only observable in the presence of certain additives. Among the compounds that were found to be effective were ethers, alcohols, pyridine, N,N-dimethylacetamide, ethyl acetate, and acetone. By contrast methyl iodide, acetonitrile, chloroform, and carbon tetrachloride were all without effect. Thus, for example, all of the ketones which became colored on irradiation in an ether-ethanol glass at 77°K. (see Table III), with the exception of the benzylchromones VIII, X, and XI, also became colored on irradiation in the hydrocarbon glass if 1-5% of pyridine or ether had been added but not if methyl iodide or chloroform were used instead. Of the three exceptional benzylchromones, VIII became colored in the hydrocarbon glass only with pyridine, and X and XI did not become colored at all, but the fact that they all were photochromic in ether-ethanol suggests that their behavior differs only quantitatively from the other compounds.<sup>19</sup>

Presently available evidence suggests that the mechanism operative at room temperature very probably involves the intermediacy of a triplet state of the ketone<sup>3,6</sup> (eq. 1-3 where  $K_0$ ,  $^1K$ , and  $^3K$  represent the



ground, lowest singlet, and lowest triplet states of the ketone, respectively, and  $E_0$  represents the ground

(18) Cf. G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964).

(19) Probably the benzylchromone XII, which was not photochromic even in ether-ethanol at 77°K., also differs only quantitatively from these other chromones since its emission behavior is unique among those photochromic compounds which fail to color under these conditions, viz., XII, XV, XXI, and XXII (see following discussion and Table III).

state of the enol).<sup>20</sup> The present low-temperature studies appear to require that at least one of these steps must have an activation energy which is readily overcome at room temperature in a saturated hydrocarbon solvent but which can be surmounted at low temperature only through catalysis by one of the above additives. The behavior of XV, XX, XXI, and XXII (Table III) seems to suggest that the intersystem crossing step (2) may be inhibited at the low temperature. Thus while each of these compounds displayed little or no visible long-lived phosphorescence at 77°K. in a hydrocarbon glass, the additives which had been found to catalyze photoenolization of the other ketones produced instead strongly increased phosphorescence intensity in this group of compounds. However, activation of phosphorescence could be induced even by certain additives which did not catalyze photoenolization. Thus only compounds having electron-donor properties appeared to catalyze photoenolization whereas even poor electron donors such as acetonitrile, methyl iodide, carbon tetrachloride, etc. (*vide supra*),<sup>21</sup> were found to activate the phosphorescence of XV, XX, XXI, and XXII. Therefore the only requirement for phosphorescence activation seems to be that the additives have a relatively polarizable structure which presumably is needed for catalysis of intersystem crossing (eq. 2) while activation of photoenolization by a donor must be due to catalysis of some other process, presumably the enolization step (eq. 3). Catalysis of eq. 3 by donors might arise through formation of a charge-transfer (presumably triplet) complex of the excited ketone with the donor which might then undergo enolization prior to dissociation.<sup>22</sup>

No matter what the exact mechanism of catalysis, the present data strongly suggest that there is a meaningful inverse relationship between the ability of a ketone to undergo photoenolization and its ability to show long-lived phosphorescence. Thus, none of the compounds that showed long-lived phosphorescence either in the presence of polar additives (XV, XX, XXI, XXII) or in their absence (III, V) photoenolized under the conditions where phosphorescence was observed (see Table III). Since  $n, \pi^*$  triplets are well known to have very short radiative lifetimes, the lowest triplet state apparently is not  $n, \pi^*$  under the conditions where phosphorescence was observed. It therefore seems probable, as has been suggested by others,<sup>2,3</sup> that photoenolization can only occur efficiently when the lowest triplet configuration is  $n, \pi^*$ .

There remains, however, to be explained (a) why XV, XXI, and XXII photoenolize at room temperature (presumably through an  $n, \pi^*$  triplet) when at 77°K. they do not react and display long-lived phosphorescence (presumably through a  $\pi, \pi^*$  triplet), and (b) what the reason is for the activation of phosphorescence

of these compounds by polarizable additives. As regards the temperature effect (a), it seems entirely possible that XV, XXI, and XXII each have  $n, \pi^*$  triplet states that are of only slightly lower energies than their  $\pi, \pi^*$  triplet states and that on lowering the temperature there is an inversion of these energy levels. This would account both for the lack of reaction and the phosphorescence at the low temperature. However, regardless of the interpretation, *the phenomenon is of important practical significance since it illustrates the dangers in the practice of utilizing spectroscopic assignments obtained at low temperature for the interpretation of photochemical reactions that are studied at room temperature.*

As for the reason for the activation of phosphorescence by polarizable additives (b), it is noteworthy that not only the photoenolizable compounds XV, XXI, and XXII but also XX, 2-acetylnaphthalene, and *p, p'*-bis(dimethylamino)benzophenone (Michler's ketone) display increased long-lived phosphorescence intensity in the presence of polarizable additives. Apparently this phenomenon must be due to catalysis of intersystem crossing (eq. 2), but why this catalysis occurs and why intersystem crossing is inhibited in the low-temperature hydrocarbon solutions of these compounds while III and IV phosphoresce strongly in the absence of any additive is not presently understood.

Returning now to a consideration of the reasons for the failure of the photoenolization reaction among some of the compounds studied, a comparison of the unreactive 2-methyl-3-benzoylchromone XVI and the photoenolizable 2-benzyl-3-benzoylchromone VIII is particularly interesting. Since the chromophores of these two compounds are virtually identical, their reactivities must be controlled by the nature of the products. However, the energies of the ground states of the two corresponding enols relative to the energies of the keto forms must be very similar and could hardly be expected to control the course of such an exothermic process as eq. 3. On the other hand if excited states of the enols were formed as intermediates, the more conjugated excited photoenol of the benzyl derivative VIII might be expected to be substantially less energetic than that of its methyl-substituted counterpart XVI. We propose therefore that, at least in the case of the chromones, and probably more generally, the key photoenolization step (eq. 3) must be elaborated as in eq. 4 and 5 to include an intermediate excited state of the



enol product. The success of the reaction would then depend both on the energy of the enol excited state being lower than that of its precursor and also on the existence of only a small activation energy in the enolization step (4).<sup>23a</sup> An indication that this interpretation may be correct is found in the requirement mentioned above (Results) that the photoenolization process must be followed by a *cis-trans* isomeriza-

(20) As will become clear in the sequel eq. 3 is not intended to imply that this process necessarily takes place in a single step.

(21) For comparison of the donor properties of various substances see G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, pp. 124, 125, 144, *et seq.*

(22) Evidence for the formation of excited charge-transfer complexes in electron donor induced fluorescence quenching has previously been described; see, *inter alia*, H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallmann and G. M. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p. 74; T. Miwa and M. Koizumi, *Bull. Chem. Soc., Japan*, 36, 1619 (1963); A. Weller in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 187.

(23) (a) These arguments can also serve to rationalize the different sensitivities toward photoenolization of the methyl-substituted 3-hexen-2-ones.<sup>2</sup> (b) The occurrence of *cis-trans* isomerization of the enolic C=C bond in a subsequent photochemical process has been excluded by the observation that the quantum yield of the photoenolization of the chromone VIII is not intensity dependent: unpublished observation by W. A. Henderson, Jr.

tion of the newly formed enolic C=C bond. Initial formation of an excited state of the enol would accommodate this requirement since rotation about this double bond would then be expected to occur prior to internal conversion to the ground state.<sup>23b</sup>

Similar reasoning based on the energies of the excited enols may be used to explain the failure of the chromones XVII and XVIII to photoenolize. This reasoning should also be justified in the case of the methoxyquinoline XX which should have an enol with even relatively high ground-state energy due to interruption of aromatic resonance of both rings. Of the remaining unreactive ketones III, V, XIII, and XIX, the naphthalene and fluorene derivatives III and V both display intense phosphorescence at 77°K. both in the presence and absence of donors and thus may fail to photoenolize because their lowest triplets are  $\pi, \pi^*$ <sup>24</sup> (*vide supra*). On the other hand, the lack of reactivity of the nonphosphorescent 2-benzyl-3-benzoylquinolone XIX as compared to its reactive isoelectronic N-methyl derivative XXI is most probably due to greatly enhanced acidity of the NH grouping of the singlet of XIX which leads to rapid deactivation by ionization.<sup>25</sup> The failure of the nitrochromone XIII to undergo photoenolization may well be related to some property peculiar to the nitro group.<sup>26</sup>

### Experimental Section<sup>27</sup>

**Deuterium Exchange Experiments.** A 50–100-mg. sample of the appropriate ketone was dissolved in 2 ml. of deuteriomethanol (CH<sub>3</sub>OD) in a Vycor glass tube (light transmission above 225 m $\mu$ ), and the system was flushed with nitrogen and stoppered. If the compound was incompletely soluble, enough dry benzene was added to achieve solution. The mixture was stirred if two phases were present. After 6–8 hr. of irradiation with a 1000-w. G.E. B-H6 lamp using a Corning No. 9863 nickel oxide filter transmitting between 250 and 370 m $\mu$ , the solution was evaporated to dryness and the resulting solid was recrystallized<sup>28</sup> (see Table I for solvents). The amount of deuterium incorporated into each sample was determined by n.m.r. analysis using the integral ratios of the aromatic to aliphatic protons. The pure starting materials and products were compared as 10% solutions in deuteriochloroform. In several cases the results were checked by mass spectrometry.

**Photochromic properties** of the ketones examined in this study were tested by irradiation of 10<sup>-4</sup>–10<sup>-1</sup> M solutions in Pyrex glass tubes using the above-described light source. The solvents used included ethanol, isopropyl alcohol, ether, acetone, acetonitrile, benzene, and cyclohexane at room temperature and 1:1 ether-

(24) The assignment of a  $\pi, \pi^*$  configuration to the lowest triplet of the 1-benzoylnaphthalene III seems reasonable in light of a similar assignment to the lowest triplet of 1-naphthaldehyde: G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

(25) Enhancement of acidity upon excitation to the singlet state is well documented; see H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 156.

(26) Possibly the nitro group interferes in these reactions by intervention of a low-energy  $n, \pi^*$  triplet involving the nonbonding electrons of the nitro oxygens.

(27) The n.m.r. spectra were measured using deuteriochloroform as solvent, and infrared spectra were taken of mineral oil suspensions unless otherwise noted. Melting points are corrected.

(28) The liquid *o*-methylbenzophenone was analyzed without further purification.

ethanol and 1:1 methylcyclohexane–3-methylpentane mixtures at both room temperature and 77°K. Compounds that were found to be photochromic at room temperature (Table II) generally displayed this property in all the solvents used at this temperature. The effect of removing oxygen from the solutions appeared to be primarily limited to decreasing the rate of the fading process.<sup>6</sup>

The effect of additives at 77°K. was determined by irradiation of a 1:1 3-methylpentane–methylcyclohexane glass containing the ketone and the additive in concentrations varying from 1 to 10%. The formation of the photoenol and changes in emission characteristics were observed visually. The effects of ether and pyridine were studied with all the ketones investigated in this study. The effects of other additives described in the text were studied principally with I (R = H), IV, XIV, and XV, although a number of experiments using other ketones were made to ensure that the observations were generally applicable. The effect of ether, pyridine, and CCl<sub>4</sub> on the phosphorescence of 10<sup>-3</sup> M 2-acetylnaphthalene and 10<sup>-3</sup> M *p,p'*-bis(dimethylamino)-benzophenone was also studied (activating light at 3650 Å.). Each of the additives studied increased the long-lived phosphorescence intensity.

*o*-Methylbenzophenone,<sup>29</sup> 1-benzoyl-2-methylnaphthalene,<sup>7,30</sup> 1-benzoylfluorene,<sup>9</sup> and 6-benzylbenzanthrone<sup>5</sup> were prepared and purified by procedures given in the literature. *o*-Benzylbenzophenone<sup>30</sup> was prepared by reaction of benzonitrile with *o*-benzylphenylmagnesium bromide, followed by hydrolysis.<sup>31</sup>

**2-Benzoyl-3-benzylbenzofuran (VII).** A solution of 1.0 g. (0.0047 mole) of *o*-hydroxy- $\omega$ -phenylacetophenone,<sup>32</sup> 0.28 g. (0.0050 mole) of potassium hydroxide, and 0.94 g. (0.0047 mole) of phenacyl bromide in 5 ml. of ethanol was refluxed for 2.5 hr., and the cooled solution was diluted with water and extracted with benzene. The dried extracts were evaporated to an oil which was chromatographed on neutral alumina. Elution with ether afforded a solid which was recrystallized from hexane to give 1.0 g. (68%) of the benzofuran as pale yellow prisms, m.p. 91–92°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>: C, 84.59; H, 5.16. Found: C, 84.59; H, 5.01.

**3-Benzoyl-2-benzylbenzofuran (VI).** A solution of 17.0 g. (0.082 mole) of 2-benzylbenzofuran<sup>33</sup> and 12.7 g. (0.090 mole) of benzoyl chloride in 50 ml. of carbon disulfide was swirled in an ice bath while 21.5 g. (0.082 mole) of stannic chloride was added in portions during 5 min. The resulting dark solution was kept at room temperature for 18 hr. and concentrated under a stream of nitrogen. The resulting black tar was partitioned between chloroform and 6 N hydrochloric acid, and the organic layer was separated and washed once with 6 N hydrochloric acid and twice with 5% sodium carbonate. The dried solution was evaporated, and the residue was crystallized from ether–petroleum ether

(29) D. J. Reiding and W. Th. Nauta, *Rec. trav. chim.*, **80**, 339 (1961).

(30) We are indebted to Mr. R. Lopresti for preparation of this material.

(31) Cf. F. A. Vingiello and M. M. Schlechter, *J. Org. Chem.*, **28**, 2448 (1963).

(32) (a) J. N. Chatterjea and S. K. Roy, *J. Indian Chem. Soc.*, **34**, 155 (1957); (b) M. O. Farooq, W. Rahman, M. Ilyas, and S. Jehan, *Ber.*, **94**, 1996 (1961).

(33) M. Bisagni, N. P. Buu-Hoi, and R. Royer, *J. Chem. Soc.*, 3693 (1955).

(b.p. 30–60°) in several crops to give a total of 6.30 g. (25%) of yellow crystals, m.p. 106–110°. Recrystallization from methanol gave pale yellow prisms, m.p. 109–111°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>: C, 84.59; H, 5.16. Found: C, 84.36; H, 5.30.

*Arylacetic Anhydrides.* Phenylacetic,<sup>34</sup> *p*-methoxyphenylacetic, and diphenylacetic<sup>35</sup> anhydrides were prepared by refluxing the corresponding acid with 2.5 times its weight of acetic anhydride for 2 hr. Distillation of the acetic acid and excess acetic anhydride *in vacuo* left the crude anhydrides, which crystallized on standing. The solids were washed with petroleum ether containing a small amount of ether and used directly in the preparation of the corresponding chromones.

*o*-Hydroxydibenzoylmethane,<sup>36</sup> *o*-hydroxy-*p*'-nitrodibenzoylmethane,<sup>13</sup> and 2-hydroxy-4-dimethylaminodibenzoylmethane<sup>37</sup> were prepared by literature procedures.

*o*-Acetylphenyl *p*-Cyanobenzoate. *o*-Hydroxyacetophenone, 13.6 g. (0.10 mole), and 15.0 g. (0.10 mole) of *p*-cyanobenzoyl chloride<sup>38</sup> were mixed in 20 ml. of pyridine. The resulting warm solution was allowed to stand for 15 min. and then poured into a mixture of ice and dilute hydrochloric acid. The resulting solid was filtered and washed with water to give 22.5 g. (85%) of the ester, m.p. 99–100.5°. One recrystallization from methanol raised the melting point to 103–104.5°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>11</sub>NO<sub>3</sub>: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.30; H, 4.45; N, 5.54.

*p*-Cyano-*o*'-hydroxydibenzoylmethane. A warm solution of 19.0 g. (0.072 mole) of *o*-acetylphenyl *p*-cyanobenzoate in 60 ml. of pyridine was treated with 6.2 g. (0.11 mole) of powdered potassium hydroxide and stirred without external heating for 1 hr. The mixture was acidified with 100 ml. of 10% acetic acid and the

(34) W. Autenrieth and G. Thomae, *Ber.*, **57**, 423 (1924).

(35) C. D. Hurd, R. Christ, and C. L. Thomas, *J. Am. Chem. Soc.*, **55**, 2589 (1933).

(36) T. S. Wheeler, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 478.

(37) D. Molho and J. Aknin, *Compt. rend.*, **259**, 1645 (1964).

(38) H. Adkins and C. Scanley, *J. Am. Chem. Soc.*, **73**, 2854 (1951).

product was filtered off and recrystallized from methanol to give 6.7 g. (35%) of the diketone, m.p. 160–162°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>11</sub>NO<sub>3</sub>: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.34; H, 4.27; N, 5.51.

*3-Aroyl-2-arylmethylchromones. General Procedure.* An equivalent amount of the appropriate arylacetic anhydride was mixed with a suitably substituted *o*-hydroxydibenzoylmethane in the presence of a slight excess of triethylamine, and the mixture was heated on the steam bath for periods of 1–16 hr. The cooled reaction mixture was taken up in ether or benzene and washed with saturated sodium bicarbonate. The dried solution was then evaporated and the residue was crystallized from ethanol or benzene. The chromones prepared by this procedure are listed in Table I.

The compounds all displayed infrared absorption near 6.0  $\mu$  corresponding to the benzoyl carbonyl and near 6.15  $\mu$  corresponding to the chromone carbonyl grouping. The n.m.r. spectra were consistent with the proposed structures.

*3-Benzoyl-2-(p-hydroxybenzyl)chromone (XI).* A mixture of 2.8 g. of 3-benzoyl-2-(*p*-methoxybenzyl)-chromone, 40 ml. of acetic acid, and 30 ml. of 48% hydrobromic acid was refluxed for 3 hr. and then poured into ice water. The resulting solid was removed by filtration and recrystallized from ethanol to give 1.5 g., m.p. 210.5–211.5° (see Table I for analysis, etc.).

*3-Benzoyl-2-(bromomethyl)chromone (XVII).* A solution of 1.91 g. (0.0072 mole) of 3-benzoyl-2-methylchromone<sup>13,39</sup> in 60 ml. of carbon tetrachloride was treated with 1.30 g. (0.0073 mole) of *N*-bromosuccinimide and the resulting mixture was refluxed for 5 hr. while irradiating with unfiltered light from a 150-w. Hanovia medium-pressure mercury arc. The mixture was cooled and filtered and then evaporated. The residual oil was crystallized from benzene–hexane and recrystallized from ethanol to give 1.72 g. (70%) of off-white plates, m.p. 141.5–144°. Two further recrystallizations raised the melting point to 147–148° (see Table I).

(39) H. Müller, *J. Chem. Soc.*, **107**, 872 (1915).